

November 16, 1865.

Lieut.-General SABINE, President, in the Chair.

In accordance with the Statutes, notice of the ensuing Anniversary Meeting for the election of Council and Officers was given from the Chair.

Mr. Bowman, Dr. Frankland, Mr. F. Galton, Sir John Lubbock, and Mr. Spottiswoode, having been nominated by the President, were elected by ballot Auditors of the Treasurer's accounts on the part of the Society.

Mr. George Robert Gray was admitted into the Society.

The following communications were read :—

- I. "Synthetical Researches upon Ethers.—Synthesis of Ethers from Acetic Ethers." By E. FRANKLAND, F.R.S., Professor of Chemistry in the Royal Institution of Great Britain, and in the Royal School of Mines, and B. F. DUPPA, Esq. Received July 13, 1865.

(Abstract.)

In a recent note * we have briefly described the synthesis of butyric and diethacetic ethers by acting consecutively upon acetic ether with sodium and the iodide of ethyl. In the present paper we have the honour to lay before the Royal Society the detailed results of one section of this research, embracing the action of sodium and the iodides of methyl, ethyl, and amyl upon acetic ether.

I. *Action of Sodium and Ethyl Iodide upon Acetic Ether.*

When acetic ether is treated with sodium at a temperature gradually rising to 120° C., hydrogen is evolved, and a thick brownish liquid produced; the latter solidifies on cooling to a yellowish mass, presenting the appearance of beeswax. On digesting this solid mass with ethylic iodide at 100° C. for several hours, a number of products are formed, which on the addition of water, may be distilled off from a residue consisting chiefly of iodide of sodium. The distillate can readily be separated into an aqueous and an oily portion. The latter then presented the appearance of a light straw-coloured oil, possessing a pleasant and fragrant odour. It was washed and then dried over chloride of calcium, and submitted to fractional distillation, by which traces of alcohol, acetic ether, and ethyl iodide were effectually removed from the other products, which now boiled between 120° and 265° C. We have described the constituents of this complex liquid under two distinct heads, viz. :—

1st. Products depending upon the duplication of the atom of acetic ether.

2nd. Products derived from the replacement of hydrogen in the methyl of acetic ether by the alcohol-radicals.

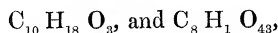
In order successfully to separate the two products from each other, and

* Proceedings of the Royal Society, vol. xiv. p. 198.

especially to disentangle their constituent compounds, it is absolutely necessary to operate upon large quantities of material. But if this be done, there is obtained a considerable quantity of the products of the first division boiling between 204° and 208° , whilst the products of the second division boil considerably below these temperatures.

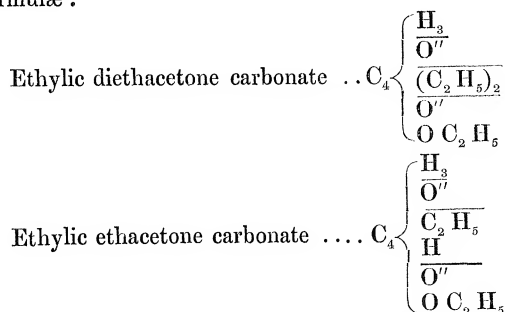
a. Examination of the products depending upon the duplication of the atom of acetic ether.

Submitted to analysis, this liquid was found to consist of two bodies of the formulæ

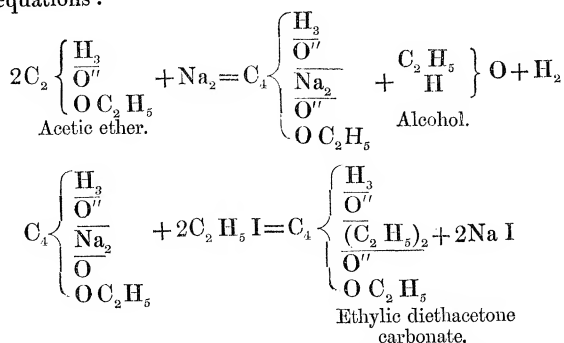


separable from each other by repeated rectification, and also by the action of boiling aqueous potash, which decomposes the second but scarcely affects the first.

From the results of the analysis, and from considerations which are fully entered into in the paper, we propose for these bodies the following names and formulæ :



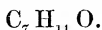
The production of ethylic diethacetone carbonate is explained in the following equations :



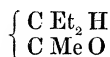
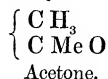
Ethylic diethacetone carbonate is a colourless and somewhat oily liquid, possessing a fragrant odour and a pungent taste. It is insoluble in water, but miscible in all proportions with alcohol and ether. Its specific gravity is $\cdot 9738$ at 20°C . It boils between 210° and 212° , and distils unchanged.

The density of its vapour was found to be 6.59. The above formula, corresponding to two volumes, requires the number 6.43. Boiling aqueous solutions of potash and soda have scarcely any action on ethylic diethacetone carbonate, but baryta-water and lime-water decompose it with great facility, as do also boiling alcoholic solutions of potash and soda. In all cases a carbonate of the base is precipitated, and alcohol, together with a light ethereal liquid, is separated.

This liquid, freed from alcohol by repeated washing with salt and water, boiled, after drying over chloride of calcium, between 137°·5 and 139° C. Submitted to analysis, it yielded results corresponding with the formula

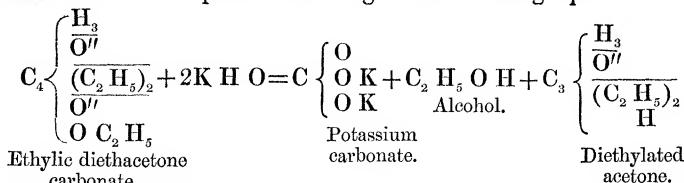


We regard this body as *diethylated acetone*. Its formula and its relations to acetone may be thus expressed :

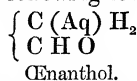
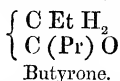
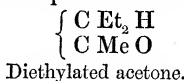


Diethylated acetone.

Diethylated acetone is produced from ethylic diethacetone carbonate by the action of alcoholic potash according to the following equation :

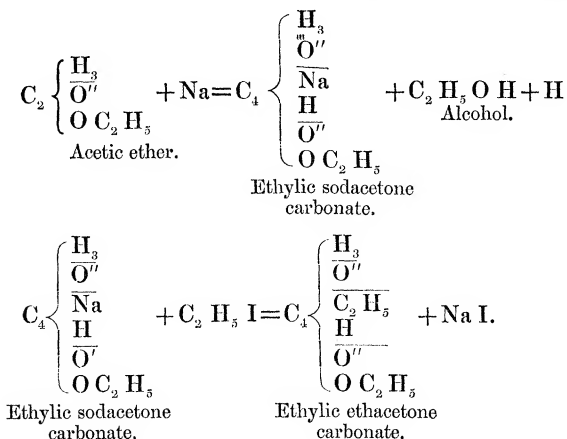


Diethylated acetone is a colourless, transparent and mobile liquid, possessing a penetrating odour of camphor, and the burning and bitter after-taste of the same substance. It is very slightly soluble in water, but miscible in all proportions with alcohol and ether. Its specific gravity is .8171 at 22° C. It boils at 137°·5 to 139° C. A determination of its vapour-density gave the number 3.86, the above formula requiring 3.93. Diethylated acetone does not oxidize in the air, neither does it reduce ammoniacal solution of nitrate of silver when boiled with it. Mixed with concentrated solution of sodium bisulphite, it forms an oily compound which scarcely exhibits signs of crystallization at 0° C. It suffers no alteration by prolonged boiling with alcoholic potash. It is isomeric with butyrene, with a ketone obtained by Fittig* in the distillation of calcium valerianate, and with cenanthol. From the first it is distinguished by its lower boiling-point (138°), butyrene boiling at 144° C., and Fittig's ketone at 161° to 164°, and from the third by its different properties, which are essentially those of a ketone and not of an aldehyde. The difference in structure of three of these bodies may be expressed with considerable certainty by the following formulæ :

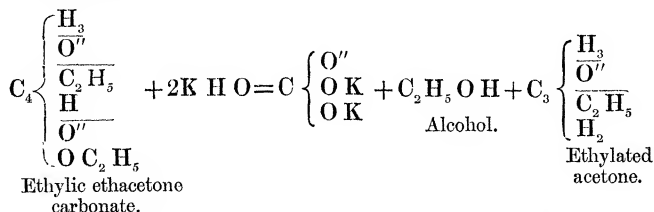


* Ann. Ch. Pharm., vol. cxvii. p. 68.

Ethylic ethacetone carbonate is produced by the action of sodium and ethylic iodide upon acetic ether, according to the following equations :



Ethylic ethacetone carbonate is a colourless and transparent liquid, possessing a very fragrant odour and an aromatic taste. It is nearly insoluble in water, but miscible in all proportions with alcohol and ether. Its density in the liquid condition is .9834 at 16° C. It boils at 195° C., and distils without decomposition. A determination of its vapour-density gave the number 5.36. The above formula requires 5.45. Ethylic ethacetone carbonate is readily attacked by boiling aqueous solutions of potash and soda, yielding carbonates of these bases, alcohol, and *ethylated acetone*, according to the following equation :

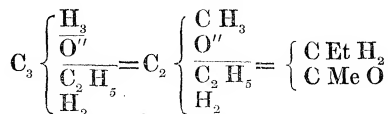


Ethylic ethacetone carbonate is still more readily decomposed by aqueous solution of baryta and by alcoholic potash, in both cases ethylated acetone and a carbonate of the base is produced.

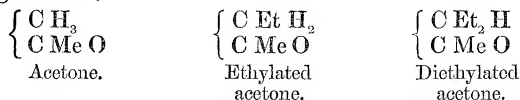
Ethylated acetone may be freed from alcohol by repeated washing with salt and water, but it is best obtained in a state of absolute purity by combination with, and subsequent separation from, bisulphite of soda. Ethylated acetone thus purified and rectified from quicklime yielded on analysis numbers agreeing well with the formula



which may be reduced to the radical type as follows :



Its relations to acetone and diethylated acetone are then clearly seen in the following formula,



Ethylated acetone is a colourless, transparent and very mobile liquid, possessing a powerful and pleasant odour, in which that of camphor is slightly perceptible. Its specific gravity is .8132 at 13° C., and .8046 at 22° C. It boils steadily at 101.5, and its vapour has the density 2.951, the above formula requiring 2.971. Ethylated acetone neither absorbs oxygen from the air, nor reduces ammoniacal solutions of silver. It yields with concentrated solutions of bisulphite of soda a compound in large and brilliant crystals, which are quite permanent in the air, and which at once distinguish it from diethylated acetone, the latter producing under the same circumstances an oily compound. Ethylated acetone is not altered by prolonged ebullition with alcoholic potash.

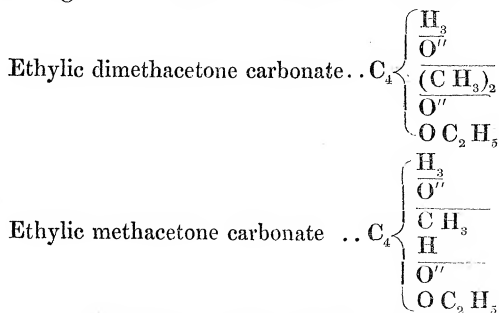
β. *Examination of the products derived from the replacement of hydrogen in the methyl of acetic ether by ethyl.*

The chief results of this examination are given in the note above alluded to*, and we have only to add that ethacetic acid is identical with butyric acid, whilst diethacetic acid is isomeric with caproic acid.

II. *Action of Sodium and Methyl iodide upon Acetic Ether.*

This reaction is conducted in substantially the same manner as that above described, and the products are completely homologous. Thus there are produced two carboketonic ethers, and an ether derived from acetic ether by the substitution of methyl for hydrogen. The latter has been already described in our previous communication on this subject.

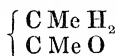
The following are the names and formulæ of the carboketonic ethers:—



* Proceedings of Royal Society, vol. xiv. p. 198.

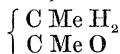
The reactions involved in the production of these bodies are exactly similar to those by which the corresponding ethylic bodies are formed.

Ethylic dimethacetone carbonate is a colourless, slightly oleaginous liquid, possessing a peculiar penetrating and pleasant odour, and a sharp burning taste. It is scarcely at all soluble in water, but readily so in alcohol and ether. Its specific gravity is $\cdot 9913$ at 16°C . It boils constantly at 184°C ., and distils unchanged. A determination of its vapour-density gave the number $5\cdot 36$, the above formula requiring $5\cdot 45$. Its remaining properties very closely resemble those of ethylic diethacetone carbonate. Boiled with baryta-water, it gives barium carbonate and *dimethylated acetone*,



Dimethylated acetone is a colourless, transparent and very mobile liquid, possessing a pleasant odour, reminding at the same time of parsley and acetone. Its specific gravity is $\cdot 8099$ at 13°C ., and it boils at $93^{\circ}\cdot 5 \text{C}$. Its vapour-density is $2\cdot 92$, theory requiring $2\cdot 97$. Dimethylated acetone closely resembles its ethylic homologue in all its chemical properties; like diethylated acetone, it is oxidized with difficulty, and does not very readily form a crystalline compound with bisulphite of soda—differing in the latter respect markedly from its isomer, ethylated acetone, and also from methylated acetone described below.

Ethylic dimethacetone carbonate and ethylic methacetone carbonate boil at the same temperature, and cannot therefore be separated by rectification; but we have prepared and examined the ketone from the second of these bodies; viz. *methylated acetone*, which has the formula



Methylated acetone is best obtained in a state of purity by combining it with bisulphite of soda, pressing the beautiful crystalline compound so formed between folds of blotting-paper to remove traces of dimethylated acetone, exposing it over sulphuric acid *in vacuo*, and then regenerating the methylated acetone by distillation with aqueous potash. The liquid so obtained, after drying over quicklime and rectification, gave analytical results corresponding with the above formula.

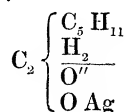
Methylated acetone is a colourless, transparent and very mobile liquid, possessing an odour like chloroform, but more pungent. It is tolerably soluble in water, and more than slightly so in a saturated solution of common salt. Its specific gravity is $\cdot 8125$ at 13°C . It boils at 81°C ., and its vapour-density is $2\cdot 52$, the above formula requiring $2\cdot 49$. Methylated acetone is identical with the ethyl-acetyl obtained by Freund* in acting upon chloride of acetyl with zinc ethyl. Methylated acetone forms a splendidly crystalline compound with bisulphite of soda, and in its other chemical properties so closely resembles ethylated acetone as to require no further description. It retains alcohol with such tenacity as to render its separation from that liquid by washing and treatment with chloride of cal-

* Ann. Ch. Pharm., vol. cxviii. p. 1.

cium almost impossible. This separation, however, is readily effected by bisulphite of soda.

III. *Action of Sodium and Amyl Iodide upon Acetic Ether.*

For this reaction the compounds of sodium derived from acetic ether were prepared as before, and were then submitted to the action of amyl iodide for several hours at the boiling-point of the mixture. When the sodium had all become converted into iodide, water was added and the supernatant liquid decanted. We reserve a complete description of this liquid for our next communication, and will here confine ourselves to the separation from it of cœnanthyllic acid, which was obtained as follows:—The crude product, after drying over chloride of calcium, was submitted to rectification, and the portion boiling between 170° and 190° C. collected apart and decomposed by ebullition with alcoholic potash. By this treatment we destroyed any ethylic amylacetone carbonate and ethylic diamylacetone carbonate that were present, and obtained a potash-salt of an acid derived from acetic acid by the substitution of one atom of amyl for one of hydrogen. The potash-salt thus obtained was distilled with excess of sulphuric acid diluted with a large quantity of water. Upon the distillate there floated an oily acid, possessing an odour resembling cœnanthyllic acid. This acid was converted into an ammonia-salt, from which a silver-salt was prepared by precipitation. After being well washed with cold water, this salt yielded numbers on analysis closely corresponding with the formula of amylacetate or cœnanthylate of silver :



We have also examined the barium-salt, which is an amorphous soapy substance. Dried at 100° C., 2715 grm. gave 1599 grm. of barium sulphate, corresponding to 34·62 per cent. of barium. Barium cœnanthylate contains 34·69 per cent. of barium. We believe amylacetic acid to be identical with cœnanthyllic acid.

The concluding portion of the paper is devoted to a discussion of the theoretical bearings of the reactions above described, and to the investigation of the internal architecture of the synthetically prepared ethers, acids, and ketones.

II. "Researches on the Hydrocarbons of the Series $C_n H_{2n+2}$."

No. II. By C. SCHORLEMMER, Esq., Assistant in the Laboratory of Owens College, Manchester. Communicated by Prof. H. E. ROSCOE. Received July 20, 1865.

From my experiments communicated to the Royal Society on the 6th of April, 1865, I concluded that the question, whether only one series of hydrocarbons of the general formula $C_n H_{2n+2}$ exists, or whether this